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Diamond; Delta-doping; SIMS; Depth resolution function

Abstract

In this work, we used the depth resolution function (DRF) of the secondary ion mass spectrometry (SIMS) to deconvolve the boron depth profile of nanometer-thin embedded diamond layers. Thanks to an isotopic change within a thin layer, where carbon-12 (^{12}C) and carbon-13 (^{13}C) are substituted, the DRF was evaluated by a self-consistent algorithm. In a second step, this DRF was used to deconvolve the boron depth profile of a double delta-doped diamond analyzed under the same ion beam condition. The expected position, thickness, and boron concentration of the embedded layers were confirmed. This technique has enhanced the SIMS performance, and the depth resolution reached the nanometer range. Interface widths of boron-doped diamond multilayers were resolved well below 1 nm/decade over a large doping range, from 3×10^{16} cm^{-3} to 1.2×10^{21} cm^{-3}, and confirmed a conformal growth layer by layer.

1. Introduction

The development of diamond growth technology has largely improved the fabrication of homo and heterostructures with abrupt interfaces such as superlattices and quantum wells [1]. Consequently, the request for a very accurate characterization has become more demanding even though the analysis of such structures is difficult and sometimes a challenge of its own (nanometer scale, low concentration of light atoms, hard material, and so on). Secondary ion mass spectrometry (SIMS) is commonly used to obtain depth profiles of dopants over many orders of magnitude in concentration. However, below 100 nm in thickness, SIMS induced ion mixing is no longer negligible; it affects strongly the depth profile measurements by broadening and distortion, so that the raw SIMS profile differs from the dopant profile, up to the point where thickness values and atom peak concentrations in multilayer stacks become erroneous. Other alternative and promising techniques like atom probe tomography [2] are not yet so commonly available, and in fact not yet demonstrated on the diamond material.

This work is dedicated to the potentiality of SIMS applied to the characterization of nanoscale diamond embedded heterogeneous structures. Diamond has several excellent properties, in most cases superior to those of other semiconductors, e.g., Si and SiC. Actually, two types of application require the availability of very thin layers (boron or nitrogen-doped) in the range of nanometer thickness, the so-called “delta structures” [3], [4] and [5], as well as the possibility to characterize such ultrathin epilayers. These applications are related to high breakdown voltage/high temperature electronic devices [6] aimed at the development of next-generation high power devices, but also to colour centers, e.g., NV centers in diamond [3] and [7], a very active research field of photonics and spintronics, more in line with the optical properties of diamond.

Technically, during a SIMS analysis, the experimental depth profile is the convolution of the dopant depth profile and of the depth resolution function (DRF) [8]. Evaluation of this DRF (which depends on the probed atom) is a key issue in nm-range secondary ion mass spectrometry. Deconvolution analysis using such a DRF provides accurate measurements on abrupt dopant depth profiles over

many orders of magnitude in concentration. The best tool to estimate quantitatively the influence of ion mixing during the SIMS analysis is the local isotopic substitution (or “isotopically pure growth”). This has already been demonstrated with silicon superlattices ($^{28}Si/^{30}Si$) [9]. The atomic substitution by an isotope is the best approach to extract the experimental response, i.e. the DRF, because it introduces only a negligible difference in mass (same recoiling effect) and ionization threshold as well as no additional crystalline strain (same lattice parameter). Once the DRF expression is known for carbon in diamond, we can apply this function to determine a genuine dopant depth profile for nitrogen, or boron, or phosphorus.

However, the requirements to record an accurate DRF are stringent. The embedded layer has to be in the same thickness range as the lattice parameter. The fabrication of such structure requires strict conditions such as flat interface, no chemical diffusion in the matter, and a single crystalline substrate [10]. Diamond epitaxial multilayer stacks fulfill these requirements.

2. Diamond sample growth

Two diamond single crystalline samples were grown in this study. A first sample, composed of a synchronized boron- and carbon-13-doped layer, was used to extract the DRF from the ^{13}C signal intensity. Furthermore, the fitting process was applied on the boron profile, in order to qualify the possibility to deconvolve the boron concentration and the layer thickness. The second sample was constituted of a double boron-doped delta layers in order to analyse the growth uniformity and the interface quality. The growth of the second sample was optimised to obtain delta layer thinness below the nanometer.

The strategy applied to grow an extremely thin embedded layer was to use a dedicated microwave plasma chemical vapor deposition (MPCVD) reactor, to work at high gas flow and at slow growth rate. This was explained in the literature, in the case of the diamond delta-doping without isotope enrichment [11]. Such equipment can grow step by step multilayer sample.

In theory, a delta structure is composed of the three layers, i.e. buffer, doped, and cap layer. In the particular case of the isotope-modulated sample, two distinct MPCVD reactors were employed in

order to grow each layer with a specific carbon isotope source (Fig. 1). Standard methane (^{12}C: 98.9 % + ^{13}C: 1.1%), diborane and hydrogen were used at Institut Néel to grow the delta layer in a vertical quartz tubular (NIRIM-type) MPCVD reactor [12] modified for the diamond boron delta-doping [5]. ^{12}C-enriched methane (^{12}C: 99.999%) was used to grow the buffer and the cap layers in a high plasma density NIMS-type reactor developed at the National Institute for Material Science [13]. In order to minimize atomic diffusion from the delta layer to the cap layer, its homoepitaxy was made carefully; a lateral growth condition was applied. The second sample was continuously grown layer by layer in a modified NIRIM-type MPCVD reactor. Etching-back plasmas were applied after growth of the boron-doped layer in order to reduce its thickness to the nanometer scale [11].

Particularly flat samples were selected to minimize surface roughness effects. The surface was ultra-polished in Japan by Syntek Co., Ltd.; the resulting surface root mean square roughness was below 0.3 nm before overgrowth.

3. SIMS profile fitting

Several authors have reported that a SIMS profile can be modelled by convolving the genuine atom profile with the SIMS depth resolution function, a response which depends on instrumental and fundamental aspects as well (convolution model). In the 90s, Dowsett et al. [10] have demonstrated that for delta-doped layers characterized by few atomic layers and hence below the SIMS resolution, an excellent approximation of depth resolution function (DRF) can be obtained by convolving a double exponential with a Gaussian distribution.

The edges of the measured SIMS signal have an exponential behavior characterized by a leading edge decay length λ_{up} (upslope during the sputtering process) and a trailing edge decay length λ_{down} (downslope). The σ parameter is related to the full width at half maximum of a Gaussian function, characteristic of the surface roughness, mostly generated by the ion beam/solid matter interaction. It depends of the incidence angle between the ion beam and the crystalline system, and the scanning velocity.

The following analytical expression of this DRF was employed for this study, similarly to past experiments performed in the silicon technology [14]:

$$\mathrm{DRF}(z) = \frac{1}{2\left(\lambda_{\mathrm{up}} + \lambda_{\mathrm{down}}\right)} \times \left\{ \exp\left(\frac{z - z_0}{\lambda_{\mathrm{up}}} + \frac{\sigma^2}{2\lambda_{\mathrm{up}}^2} \right) \times \left[1 + \frac{1}{\sqrt{2}} \cdot \mathrm{erf}\left(\frac{-(z - z_0)}{\sigma} - \frac{\sigma}{\lambda_{\mathrm{up}}} \right) \right] + \exp\left(\frac{-(z - z_0)}{\lambda_{\mathrm{down}}} + \frac{\sigma^2}{2\lambda_{\mathrm{down}}^2} \right) \times \left[1 + \frac{1}{\sqrt{2}} \cdot \mathrm{erf}\left(\frac{z - z_0}{\sigma} - \frac{\sigma}{\lambda_{\mathrm{down}}} \right) \right] \right\}$$

, where z_0 represents the position of the delta layer. This expression has the advantage to be simple to use. The procedure describing the extraction of the DRF and the removal of the ion mixing effect in a boron depth profile is given on Fig. 2.

3.1. Initialization

The initialization (arrows labeled “Init.” on Fig. 2) was used to extract the set of variable parameters (λup, λdown, and σ) and to localize the position z_0 of the layer. In practice, parameters λ_{up}, λ_{down}, and σ were evaluated separately, by local fits, in order to initialize the self-consistent fitting process. In agreement with many other works in the literature regarding SIMS depth profiling of delta-doped distributions, the edges of the measured isotopes signals have an exponential behavior characterized by an upslope length λup and a downslope length λdown. Their initial values were measured on 3–4 points, on the 1×10^{17}–1×10^{20} cm^{-3} range. The initial value of σ, more dependent on the surface roughness, was measured by 3D optical microscope to lie within the 0.1–1 nm range.

3.2. Box-shaped profile

Once the set of parameters initialised for the DRF, the next step was to determine the box-shaped profile geometry, characterized by a maximum signal intensity I_{max} and a thickness δ. If the efficiency to incorporate ^{12}C and ^{13}C is the same, and the diffusion of carbon isotope in the diamond lattice at the growth temperature (900–1000 °C) does not occur, then the isotopic layer presents a constant and uniform concentration of isotope (in our case, ^{13}C). This atomic distribution is then characterised

by a maximum of concentration and a finite thickness. The corresponding profile can be approximated by a box-shape (i.e. generated by two opposite and shifted Heavyside step functions) since interfacial rising and falling concentrations of isotope were below the depth sampling, i.e. sharper than 0.25 nm/decade in this experiment.

In this model, considering a very thin layer (below 20 nm), the integrated intensity (area) under the ^{13}C depth profile curve is the product of the ^{13}C concentration in the solid phase (precisely known from the gas composition) by the thickness of the delta layer. So, the thickness δ has been deduced, after integration, from the ^{13}C data. This method is more difficult to assert in the case of the doping by chemical impurities, because of the inexact incorporation efficiency and the possible lattice deformation.

3.3. Depth resolution function

DRF and box-shaped profile are convoluted, from the surface to the bulk, in same way as the SIMS analysis. Self-consistently, the convolution product thus obtained is compared with the original SIMS depth profile, in order to generate a residual. By adjusting step by step each parameter of the DRF, the residuals level is the reduced. Once this level is satisfying a non-reducible value, the loop is opened and the set of parameters describing the DRF can be extracted.

The carbon isotope profile was fitted by approximately 100 iterations in order to minimize the residual level and the calculation time. The best fit of the DRF from the ^{13}C signal measured on a synchronized boron/^{13}C multilayer structure was plotted on Fig. 3, with a tolerance of 0.3 nm on parameters in order to remain the residual misfit below the percent. In practice the misfit reduction seems to be limited by the noise level at high and at low intensity.

The set of values were in a good agreement with physical parameters. As reported previously [15], the ion-mixing was simulated by ion-recoil of carbon atoms induced by the Cs^+ primary ions beam in a Monte-Carlo method algorithm [16]. The obtained value was similar to the width of the broad trailing edge (λ_{down} = 3.03 nm). In addition, the rising exponential component (λ_{up} = 0.90 nm) of the

DRF was compatible with the observed backscattering. The σ parameter value was effectively found of the same order than the roughness (σ = 0.55 nm).

The DRF is used in a second step, in order to feedback the procedure to deconvolve the SIMS signal. The resulting profile appears box-shaped and modulated by the noise.

3.4. Boron depth profile

The boron depth profile was fitted with the extracted DRF of ^{13}C and a trapezoid-shaped atomic distribution. At first, the atom distribution was taken as a box, with the same thickness δ employed in the previous ^{13}C fitting. The maximum intensity was calculated from the integrated area under the boron signal intensity curve and δ.

The input distribution shape is modified step by step from a box to a trapezoid, which involves an upslope and a downslope, to reduce the residual level. At each step, the maximum intensity was adjusted in order to keep the integrated area constant. Slopes are the consequence of the interfaces width. Such interfaces have a finite thickness, directly linked to some differences between the crystal growth (carbon incorporation) and the doping. Boron and carbon atoms show a difference in their bonding kinetics. However, the sampling must be rich enough to analyze these interfaces with accuracy.

Fig. 4 shows the SIMS boron concentration profile (P_{SIMS}^{11B}) together with the fitted curve from the convolution of the ^{13}C DRF by the input distribution function. For convenience in Fig. 4, the signal intensity was converted into atomic concentration from a calibrated sample. The contribution of the ion mixing on the boron depth profile was removed by plotting the distribution profile, converted into atomic concentration, modulated by the noise deduced from the residuals.

The same procedure of boron profile fitting was applied on the second sample composed of a double boron-doped delta layers (Fig. 5). The related delta-doping technique has been optimized to build extremely sharp interfaces on the boron profile [5] and [11].

The DRF extracted from the ^{13}C was used once again in the fitting process, considering the same ion beam conditions and the equivalent surface roughness. The result confirmed the expected values for

the position, the thickness, and the atomic concentration for both boron-doped delta layers. The expected thickness was below 2 nm for d_1 and below 1 nm for d_2, with a boron concentration closed to 1.2×10^{21} cm^{-3}. However for this sample, the thickness of delta layers was in the same order than the depth sampling step. For this reason, it was not possible to measure interface thickness. The treatment was strongly limited by the sampling. The use of a lower ion beam energy would have allowed us to reach an adequate resolution for the direct study of the interfacial chemical transition.

4. Discussion

The deconvolved boron profile of the first sample was found to be 5 to 7 times sharper: the initially measured 1.5 nm/decade rising edge became 0.3 nm/decade (see Fig. 6). The best fit seemed to justify the presence of a finite thickness for the interface located between boron-doped and intrinsic diamond layer. Nevertheless, such interface thickness was composed of two points only. The sampling (Δz = 0.9 nm) was not rich enough to really conclude about an exponential or linear dependence on the doping transition.

In addition, because of the low sampling rate, it is not possible to conclude if the point found at the interface on the ^{13}C profile was in or out of the noise level. This might indicate, for example, an error in the layer position z_0. On one hand, a way to enhance the sampling is to apply a lower energy ion beam, or to detect less ion types. On the other hand, the isotopic detection becomes more difficult at low energy, because of the decrease in the sputtered matter quantity. In parallel, other effects like sputter-related distortions and matrix effects are still present, but they seem to be weak enough to collect adequate information on the structure. The fact that a sub-nanometer width could be measured on a nanometer-rough epilayer suggested that the 3D features associated to the roughness at the deepest interface of the delta-doped layer were overgrown in a conformal way by this layer and by the cap layer, and then sputtered away in a conformal way during SIMS profiling.

Fig. 7 focuses on the response to a delta layer measured under different primary ions beam energy in a SIMS Cameca IMS 7 f. In this case, primary ions were O_2^+ and secondary analysed ions were positive instead of Cs^+ and negative secondary ions. With a 46° incident angle, the depth sampling

(Δz) was 1.8, 0.9 and 0.3 nm for an interaction energy of 5, 3 and 1 keV respectively. By keeping a constant ratio between the primary ions energy and the extraction voltage, the incident stayed constant. Then, energies and incidence angles can be independently tuned in order to enhance the depth sampling.

The inset in Fig. 7 points out an increase of both the upslope (λup) and the downslope (λdown) lengths as a function of the primary ion energy only. This is a direct consequence of ion mixing. When the ion beam has more energy, the recoil and its induced scatter are expanded in the volume, increasing the decay lengths at the edges. The analysis with different ion energies modified the peak concentration and the peak width, whereas the integrated area remained the same. The λup and λdown measured on d_2 were identical on the layer d_1, which confirms a conformal growth layer by layer and a conformal sputtering during the analysis.

However, other techniques are always necessary for an accurate calibration of the depth scale. For example transmission electron microscopy (TEM) can be very useful to check on local variations and to provide internal standards, such as the position of the layers and their thicknesses. In particular, High Angle Annular Dark Field scanning TEM observations of diamond epilayers cross-sections have been recently shown to be sensitive to the presence of boron concentrations above 10^{20} cm^{-3}[17] and to provide a quantitative analysis tool with nanometer resolution [18]. We plan to apply such a technique to the double delta-doped sample shown in Fig. 5.

5. Conclusion

By a local isotope enrichment of diamond, we were able to extract the instrument response of the SIMS and to characterize the incorporation of both carbon and boron atoms. These treatments allowed to increase the SIMS resolution, in order to subtract the broadening and the distortion induced by ion-mixing and to reach the nanometer-range. This procedure yielded a more reliable characterization by SIMS of nanometer thin diamond embedded layers containing specific impurities over a wide range of concentrations. The conformal growth layer by layer in the delta-doping was confirmed. For these reasons, the isotopic diamond delta structure is a powerful calibration tool for

SIMS. Once the SIMS response is known for a specific analysis condition, the enhanced resolution allows in principle to determine the position and the thickness of any doped layer, however thin, if the depth sampling by SIMS is frequent enough.

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Figures

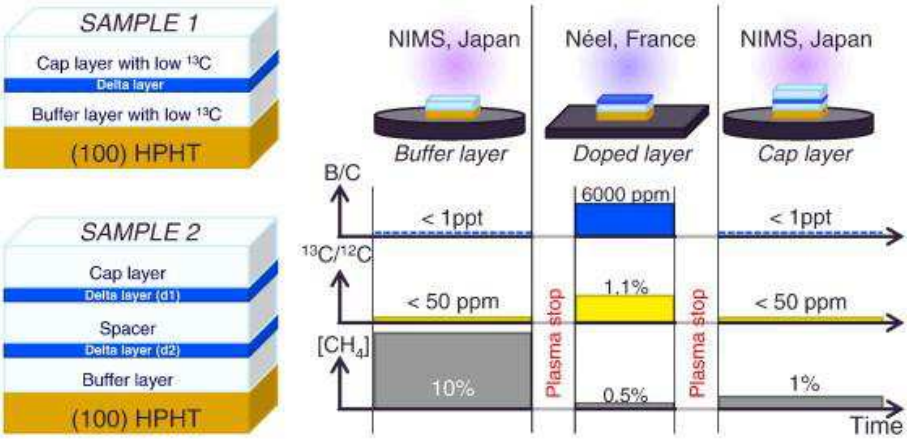

Fig. 1.
Stacking structure of samples 1 and 2 together with the flowchart used to grow sample 1. One MPCVD reactor employed low ^{13}C methane source for intrinsic growth and another allowed a boron doped growth with a standard methane source.

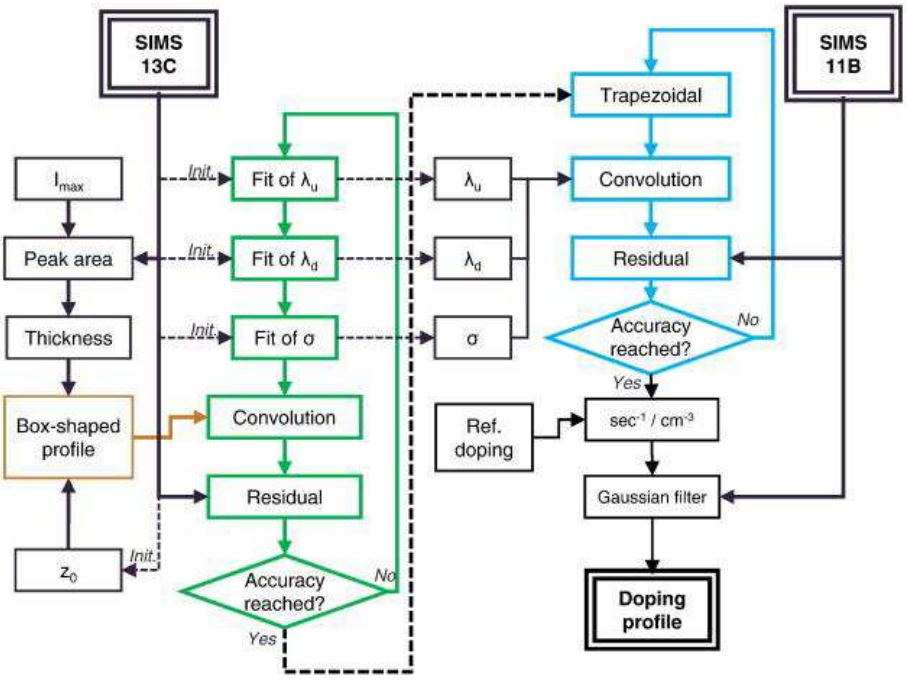

Fig. 2.
Block diagram of the global procedure containing four sub-routines. The first one built the box-shaped profile used by a self-consistent DRF extraction from the isotopic carbon depth profile (green loop), then another loop (in blue) fits the boron depth profile with the extracted DRF, and the last one plots the deconvolve boron depth profile. I_{max} corresponds to the signal intensity of the natural ^{13}C abundance found in the diamond.

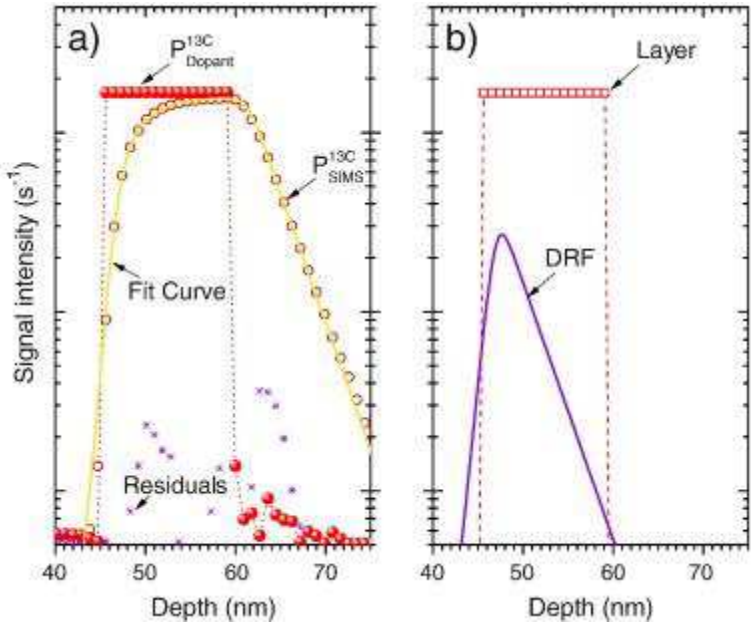

Fig. 3.

Carbon-13 depth profiles (14.5 keV Cs^+, incident angle 27°) and its related DRF in the diamond multilayer structure. (a)The SIMS intensity depth profile (P_{SIMS}^{13C}), represented by red circles, was fitted (yellow line) by the convolution of the DRF (solid purple line), and square input signal (red square) plotted on (b). The ^{13}C profile (P_{Dopant}^{13C}) plotted as light red dots illustrates the feedback of the procedure.

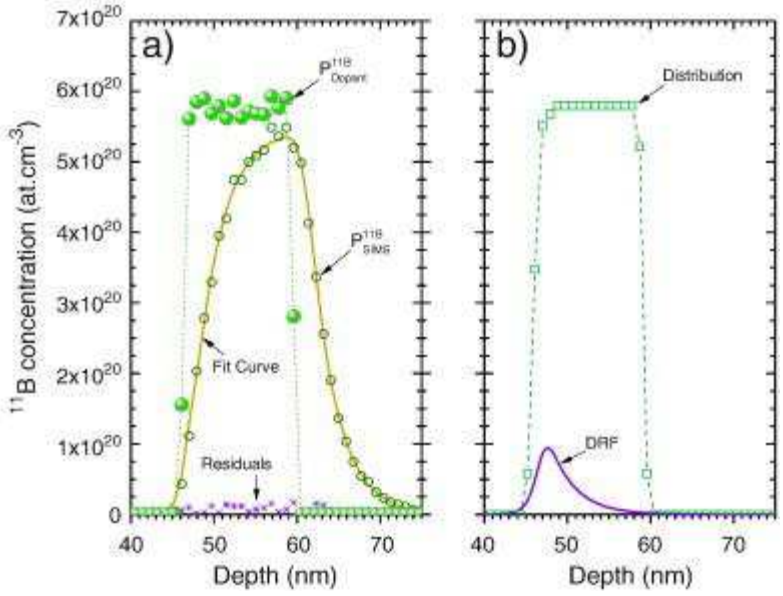

Fig. 4.

Boron-11 depth profiles (14.5 keV Cs^+, incident angle 27°) and its corresponding data treatment. (a) The SIMS boron concentration profile (P_{SIMS}^{11B}) represented by green circles, was fitted (orange line) by the convolution of the DRF (purple line), and a modulated input signal (green square) plotted on (b). The boron dopant profile (P_{Dopant}^{11B}) plotted as light green dots illustrates the result of the ion mixing removal.

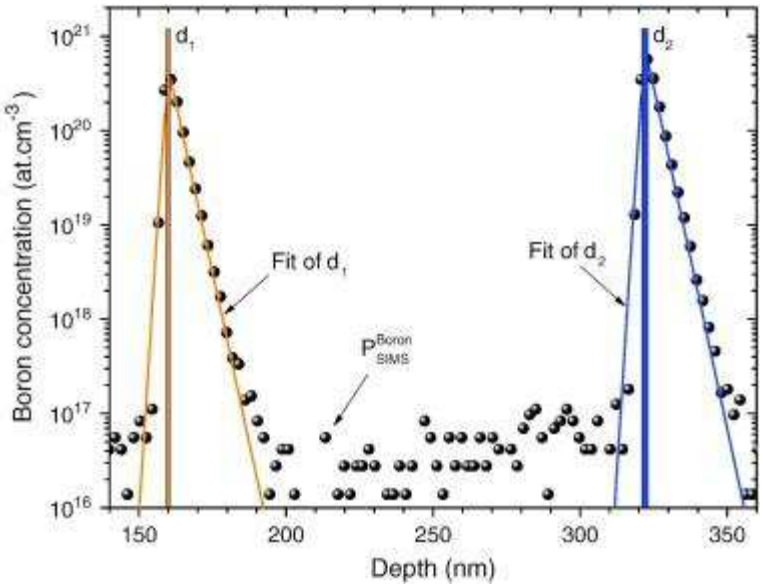

Fig. 5.

Boron depth profile (14.5 keV Cs^+, incident angle 27°) of a sample containing a double delta layer together with the corresponding data treatment. The SIMS boron depth profile (P_{SIMS}^{Boron}) represented by black dots, was fitted (orange and blue lines) by the convolution of the DRF with a modulated input signal. Both orange and blue boxes illustrate the expected position, thickness, and atomic concentration of the boron-doped delta layers (1.2×10^{21} cm^{-3}, $d_1 > 1$ nm, $d_2 > 2$ nm).

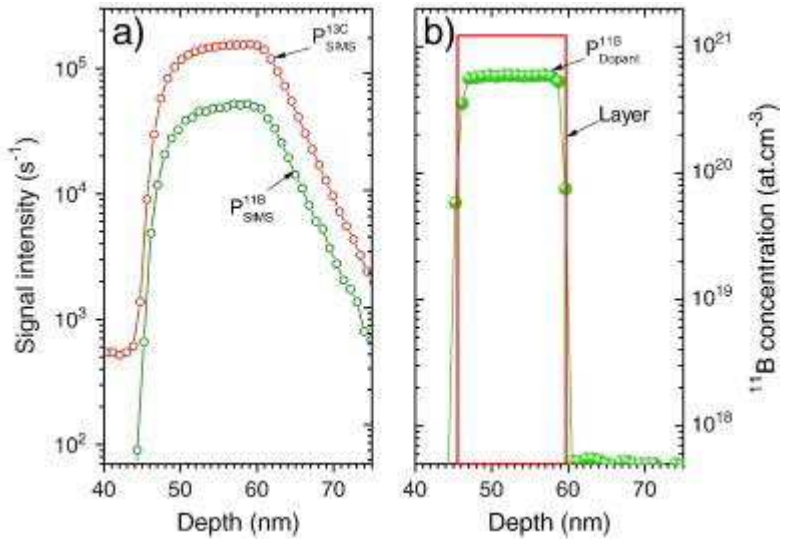

Fig. 6.

Boron and carbon-13 SIMS depth profiles of the first sample before and after treatment. (a) Initial ^{11}B and ^{13}C plotted in green and red open circles respectively. (b) Final ^{11}B depth profile (green dots) with a box indicating the position of the delta layer.

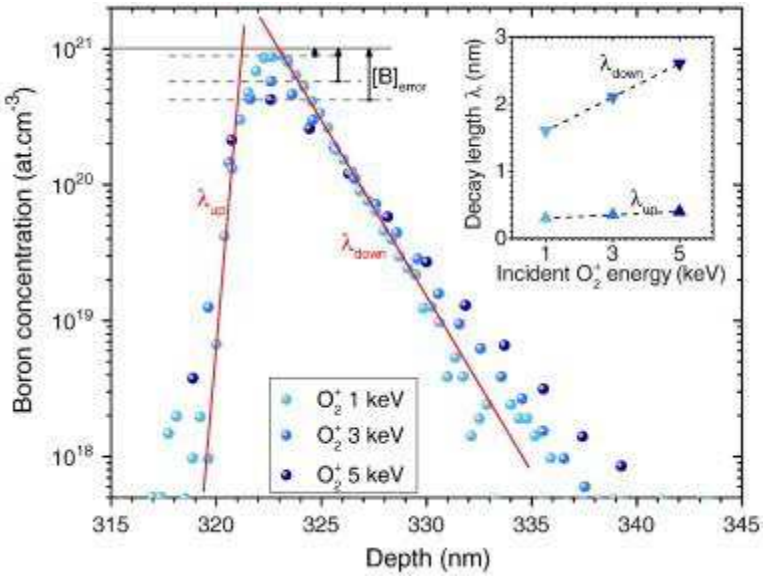

Fig. 7.

Boron depth profile recorded with O_2^+, incident angle 46°, at three different energies on the layer labelled d_2 on the Fig. 6. The inset shows the behaviour of the upslope (λ_{up}) and the downslope (λ_{down}) of the boron profile as a function of the primary ion energy.